

12

EUROPEAN PATENT APPLICATION

21 Application number: 82300098.9

22 Date of filing: 08.01.82

51 Int. Cl.³: B 65 B 55/19
B 65 D 81/26, A 23 L 3/34
B 32 B 27/18, C 08 K 3/30

43 Date of publication of application:
20.07.83 Bulletin 83/29

64 Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

71 Applicant: AMERICAN CAN COMPANY
American Lane
Greenwich, Connecticut 06830(US)

72 Inventor: Farrell, Christopher J.
431 S. Evergreen
Arlington Heights Illinois(US)

72 Inventor: Tsai, Boh C.
101 Adler Court
Rolling Meadows Illinois(US)

74 Representative: Harvey, David G. et al,
Graham Watt & Co. Riverhead
Sevenoaks Kent TN13 2BN(GB)

54 Oxygen-absorbing structures for protecting contents of containers from oxidation, containers embodying such structures and method of protecting oxidation-susceptible products.

57 A comestible container has a wall or envelope made from a plastics multilayer structure in which one layer is an oxygen barrier to guard against ingress of oxygen. The structure also comprises an activatable oxygenphilic substance, e.g. to deliquescent sulphite, between the barrier layer and the container contents or comestible, this substance being protected against moisture reaching it at least from the contents by a polymeric layer impermeable to water at normal storage temperatures but permeable thereto during filling the container or retorting it for sterilizing its contents. Wetting of the substance changes it from a passive state to the oxygenphilic state whereupon it commences fixing the oxygen in a chemically-bound state. A similar activatable structure can serve as an oxygen-scavenging insert for a container, and comestibles can be protected by sealing them in their containers followed by activating the substance to its oxygenphilic state.

OXYGEN-ABSORBING STRUCTURES FOR PROTECTING CONTENTS OF
CONTAINERS FROM OXIDATION, CONTAINERS EMBODYING SUCH
STRUCTURES AND METHOD OF PROTECTING OXIDATION-
SUSCEPTIBLE PRODUCTS.

5

The present invention relates to oxygen-absorbing structures for protecting contents of containers from oxidation, containers embodying such structures and method of protecting oxidation-susceptible products.

10

This disclosure relates to improved polymeric materials designed for packing comestibles and the like, and to containers made from such polymeric materials. Containers used to pack foods are often subjected to aggressive processing conditions e.g. during retorting for purposes of sterilising. Retortable
15 containers and their methods of manufacture are disclosed in our International patent applications filed under the PCT and published under the Numbers WO81/00230 and WO81/00231 on 5th February, 1981 (after the
20 priority date claimed in the present application). The invention the subject of this application is applicable to the subject matter disclosed in each of the aforesaid International publications.

25

Multilayer blow molded polymeric containers having barrier layers to reduce the permeation of oxygen through the wall of the container for protecting

food or beverage packed therein against oxidation have already been proposed. The problem of oxygen permeation is well recognised and is mitigated by a suitable barrier material. Moreover, such barrier materials have been used or suggested in multilayer constructions in connection with oxygen scavenging systems in order to absorb any oxygen which might pass through the barrier or remain in the head space above the packed and processed food or beverage. More particularly, U.S. Patent No. 4,048,361 discloses a food container formed with a barrier material inside of which is a carrier layer containing a "getter". The getter may be an absorbent for any gas which permeates the barrier layer. An alternative approach includes a barrier layer on both sides of the carrier layer whereby oxygen leaving the food or coming from the outside will be slowly absorbed by the getter. The patent deals in generalities as far as concerns the particular getter and is more specific regarding container shape or construction.

U.S. patent No. 3,586,514 discloses the use of antioxidizing agents mixed with a plastics barrier layer to reduce the permeation of oxygen to beer within a container.

U.S. patent No. 3,429,717 discloses a barrier

comprising Saran in a film sandwich with an antioxidant uniformly distributed between the layers of SARAN.

SARAN is a Registered Trade Mark. This patent teaches that the antioxidant should be selected
5 depending upon the film, the product to be contained and the light and heat conditions to which the package will be exposed.

U.S. patent No. 4,113,652 teaches that the presence of ammonium salts or water in an oxygen scavenger can
10 lengthen the period before the oxygen scavenger becomes effective. Increasing the amount of water or ammonium salts in the oxygen scavenger will extend its period of latency. This patent only teaches a period of latency up to fifty hours. As will be appreciated when the
15 present disclosure is fully understood, such a latency period is impractical from the standpoint of commercial reality for many food containers.

Various oxygen scavengers are known in the art. U.S. patent No. 2,825,651 discloses an oxygen remover
20 system which includes hydrates, for example, an anhydrous sodium sulfite catalyzed by copper sulfate pentahydrate. Such an oxygen remover is included as a pellet inside a protective package for placement in the container head space. The problems of putting
25 this patent into practice are pointed out in U.S. patent No. 4,113,652.

More germane to multilayer containers is U.S. Patent No. 4,041,209. This discloses an aqueous solution of a reducing sulfite salt disposed between a high barrier outer layer and a low barrier inner layer, an
5 arrangement permitting oxygen to permeate outward from the head space, so that the solution can react with the permeated oxygen and thereby retard inward oxygen flow from the outside. This patent neither teaches nor suggests controlling or triggering the solution.

10 A successful oxygen scavenger system must remain passive or inert, in order to preserve its oxygen scavenging capacity, until such time as food is sealed within the container. Containers often sit empty in warehouses for several months before use. There is a
15 need for means by which the scavenger contained in a multilayer container will be maintained passive until such time as the oxygen scavenging activity is most beneficial. The patent literature does not cater for the need to which the invention as claimed is directed.

20 The present invention provides an oxygen-absorbing structure for use in protecting the contents of containers against oxidation, wherein the structure includes an oxygen barrier layer which is substantially impermeable to the flow of oxygen therethrough, characterised by a
25 composition disposed in operative relation to at least one of the opposite surfaces of the oxygen barrier, which has a

first state wherein said composition is substantially passive and will not absorb oxygen and has a second oxygenphilic state wherein it chemically combines with oxygen, and means disposed in protective relation to the composition which selectively permit a change from ^{the} first passive state to the second oxygenphilic state. This structure can form the basis of a packaging material or container.

The invention also provides a plastics structure having enhanced resistance to oxygen transmission therethrough, characterised in that the structure includes at least one layer of a polymeric substance which includes a composition which, in a dry condition, is substantially passive and will not absorb oxygen and which, in a moist condition, is activated to an oxygenphilic state for scavenging oxygen in the course of transmission through the structure.

This structure can be employed as an insert or chip which is simply placed in a container or package to protect the contents after activation to the oxygenphilic state. No oxygen barrier is essential in this case.

The inventive structure can be embodied in a blow-moulded container. Such a container can be characterised by a wall including an outer olefinic

- layer, an oxygen barrier layer, a polymeric layer including the said composition and an innermost olefinic layer, the olefinic layers or a further layer or layer of the wall being impermeable to moisture for
- 5 protecting the said polymeric layer therefrom at temperatures below retorting temperatures, but being permeable to moisture at the latter temperatures for activating the said composition to an active, oxygenphilic state.
- 10 Also according to the present invention, there is provided a method of protecting an oxidisable product from degradation through oxidation in storage, characterised by the steps of fashioning a container from a plastics structure which has at least one layer
- 15 of a polymeric substance including a moisture-responsive material which is activatable, to an oxygenphilic state to absorb oxygen, under predetermined conditions, filling the container with the product and hermetically sealing the container about the product,
- 20 and subjecting the sealed container to high levels of moisture for a preset period of time to activate the said material to absorb oxygen within the container.

The invention will now be explained in detail by way of example.

- 25 This invention embodies an oxygen scavenger which

can be successfully activated simply and conveniently at the precise moment when its greatest need begins, and affords simple, reliable container constructions of multilayer polymeric form which are low in cost.

5 A composite wall construction for a polymeric container suitable for comestibles can be constructed from a plurality of layers each of which is selected to perform particular functions. The outer and inner layers are usually structural and protective layers
10 chosen to exclude the outside elements and to contain the comestibles, respectively. Between these layers are materials designed to control the unwanted permeation of oxygen. The outermost layer which is designed to impart structural integrity to the
15 construction, can be an olefinic thermoplastic material for its low cost, easy formability and physical characteristics. Similarly, the innermost layer also has a structural function and can likewise be fashioned from materials compatible with comestibles,
20 low in cost and easily formed.

 In between the two structural layers an oxygen barrier thermoplastic layer is located. Suitable barrier materials, may include ethylene vinyl alcohol co-polymers, such as EVAL produced by Kuraray of
25 Osaka, Japan, Saran and like materials having low

permeability with respect to the transmission of oxygen. EVAL is a Registered Trade Mark. It is advantageous to sandwich the oxygen barrier layer between a pair of outer and inner protective layers to provide a combination of packaging properties. Between the barrier layer and its neighbouring layers an adhesive material can be included to assure proper integrity between the said outer and inner layers and the barrier layer.

It is recognized that comestibles packed in for instance metal containers by conventional methods with hermetic double seamed ends will include a certain amount of head space gases and entrained oxygen, and the latter will react with some comestibles.

It is desirable to keep the head space gases to a minimum, to provide reliable end closing with hermetic seals, and also important to minimize the amount of oxygen present which can react with the container contents. Oxygen permeation into plastics containers is an additional concern not of importance with metal can manufacture. Thus, an oxygen absorbing system to protect comestibles may be required, especially for plastics containers.

Minimizing oxidation of the comestibles will help to prevent their degradation. Changes in colour,

nutritive value and flavor may be associated directly with degradation due to oxygen combining with the comestibles. In a multilayer plastics container a system to absorb oxygen is of extreme importance because, however excellent, an oxygen barrier only reduces the permeation of the oxygen into the container. A system which will absorb oxygen that passes through the barrier, and which is located between the barrier and the comestible is thus desirable. More particularly, an oxygen absorption system having a greater affinity for oxygen than the comestibles is desirable. Ideally, such a system should be capable of absorbing oxygen faster than the comestibles as well as having a stronger affinity for oxygen than the comestibles.

15 The oxygen absorption system should not be activated before the comestibles are packed. So, containers having an oxygen absorbing system should be capable of being made and stored with the oxygen absorbing system in a passive state until the precise

20 time at which the oxygen absorption is required, at which time the system will be activated. Without a triggerable absorption system having passive and active states, severe depletion of its usefulness could occur during empty storage prior to packing. The

25 benefit of any oxygen absorption system without

triggering would be limited and would necessitate prompt use of the container following its manufacture. Such a limitation is impractical in connection with commercial use and procedures for hermetically packaging of comestibles.

An oxygen absorption system having a controllable chemical behaviour is desirable. One such system includes a palladium catalyst to combine hydrogen and oxygen in the container to form water. Patent No. 4,125,632 discloses a system of this type, which is triggered by flushing the container with a gas mixture including hydrogen. Such a system as this is expensive to realise due to the cost of palladium and the extra process step needed for activation.

The present invention seeks to make use of the commonly used filling and process equipment and operations, or preferably the normal retort operation after filling, to trigger an oxygen absorption system. Desirably, activation is not occasioned merely by filling the container. This system can retain its passive state until triggered, for instance, by the sterilization procedures used after packing and during processing.

The system can involve triggering by activation by the ingress of moisture through the walls of the multilayer polymeric container. This ingress may occur during packaging, processing or sterilization. Elevated temperature during packing or sterilization is a secondary variable which speeds up permeation of water into the

oxygen absorber to activate it. Heating for activation is often desirable and in some cases may probably be a necessary step. More specifically, the oxygen absorber when dry is passive but upon contact with moisture
5 resulting from normal processing it becomes activated and begins to react with oxygen.

In the past antioxidants have been added to polymeric resins to be formed into containers, and to
10 the materials to be contained therein, to inhibit oxidation. It is also known that certain antioxidants also have an ability to react with oxygen, but usually only to a very limited extent. The differences between direct oxygen absorption and the action of
15 typical antioxidants is relevant to the present invention, which seeks to use a direct oxygen absorber in contrast to most of the earlier work which used antioxidants such as propyl gallate, and butylated hydroxyanisole, di-tertiary-butylparacresol (see U.S.
20 Patent No. 4,048,361). It is important to appreciate that typical antioxidants operate in a manner different from direct oxygen absorbers. More specifically, antioxidants are usually present in small percentages to terminate the degradation process of the material
25 into which it is mixed i.e., the plastics package itself or the contents. A direct oxygen absorber as used in this invention is capable of reacting at a significant rate with a much larger amount of oxygen

than antioxidants would and is also employed in relatively large concentrations. The chemical distinction is that oxygen absorbers react chemically only with oxygen and, while antioxidants may react with molecular oxygen, the primary action of an antioxidant is to interfere with the free-radical chemistry involved in oxidative degradation.

The concept of triggering is appreciated only in part by the U.S. Patent No. 2,316,804 where materials which do not have antioxidant activity when initially applied can, in the presence of elevated temperatures and organic packaging compositions, develop marked oxygen scavenging effects. These materials are inappropriate for containers formed by melt extrusion, however, since the high temperatures of manufacture would activate the oxygen absorption prematurely.

The preferred embodiment of this invention consists of five layers of thermoplastic material, the outer and inner layers being either polyolefinic or olefinic and the innermost layer being an oxygen barrier layer. Between the barrier and olefinic layers are adhesive layers to assure structural integrity. Either or both adhesive layers may include an oxygen absorbing system. Locating the oxygen absorbing system between the oxygen barrier and the comestible

is preferred. A number of such absorbing systems could be used in the adhesive. The choice of system is dependent upon the particular process conditions for the container and the amount of oxygen absorption desired.

5 The preferred multilayer container has olefinic outer and inner layers resistant to the transmission of water vapor at room temperature, but at elevated temperature, e.g. during retorting, they permit water vapor to permeate into the oxygen absorbing system.

10 It is the water vapor which is the triggering agent.

 The patent literature discloses systems for inclusion in a package within a container, for reacting in the presence of the moisture in the food, see, for example, German Offenlegungsschrift 28 27 247 published January 4,
15 1979. Such disclosures recognise the potential of a wet sulfite salt for oxygen absorption. According to the German OS 28 27 247 the sulfite salt is wetted by a deliquescent salt with which it is mixed. This patent document teaches the use of an at least three component
20 scavenging composition. The document does not recognise nor suggest that potassium sulfite is itself a deliquescent substance. However, the necessary water is introduced by either using the hydrated form of the salt or by contact with water in the food. There is no specific
25 teaching of triggering by the controlled application of water to activate the oxygen absorber, nor any appreciation of the discovery that the water vapor permeability of a container wall protecting the sulfite salt can become 1,000 times greater by raising _____

its temperature from 70° to 250°F, (21° to 121°C)
as is the situation when polyethylene and polypropylene
are used as the inner and outer layers. Moreover,
such disclosures do not teach that other temperature
5 ranges or process conditions will achieve triggering
with other structural layer resins.

The structures according to the present invention
contain compositions which become oxygenphilic and
react with oxygen when they have dissolved by absorbing
10 permeated water vapor. Some water-soluble salts can
become highly oxygenphilic in this deliquescent state.
A deliquescent state as used herein refers to the
condition of chemicals which are either in the process
of dissolving, or have dissolved, by absorption of
15 moisture vapor. While almost all inorganic salts
deliquesce when the relative humidity approaches 100%,
this invention is best practiced with chemicals (called
deliquescent salts) which deliquesce at lower humidities,
i.e. below about 85%.

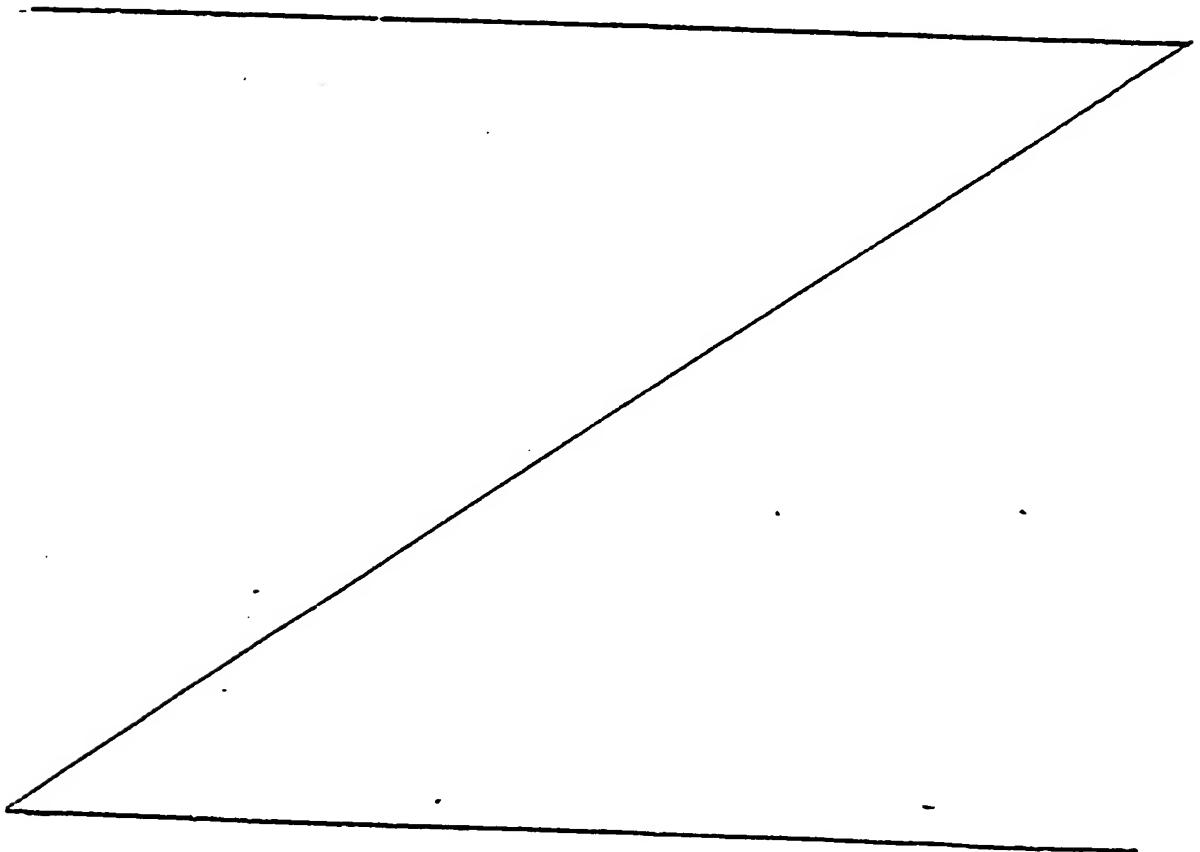
20 A deliquescent composition consists of at least
one deliquescent salt and a material which absorbs
oxygen when wetted. Deliquescence and oxygen absorption
may both be properties of a salt, as in the case of
potassium sulfite; alternatively these properties may
25 be supported by an interacting mixture of salts such

as potassium acetate and sodium sulfite. A dry composition in the container wall can come to a deliquescent state when water vapor permeates through during the retorting stage. Afterwards the moisture is trapped by the walls because their ability then to transmit moisture falls a thousand fold upon cooling. The triggering is, therefore accomplished by this combination.

Potassium sulfite is an excellent material to use in this invention as an oxygen absorber because of its deliquescence and its oxygenphilic character is exhibited only in the wet state. Potassium sulfite may be used alone or with other deliquescent salts, especially those which deliquesce at lower relative humidities to influence the triggering time. There is no problem in using potassium sulfite in connection with food containers as potassium sulfite is an approved food additive (by the FDA for instance).

The invention can be practised in the manufacture of multilayer polymeric containers by injection or extrusion molding techniques or by thermoforming. Such plastic multi-layer containers can then be sold to food and beverage packers without concern that the oxygen absorption system will be degraded during the time between manufacture and use. More specifically, the preferred

structure has an olefinic layer protecting the oxygen absorber from moisture so that it will not become highly oxygenphilic until it is retort processed. Packing a wet comestible in a container of the preferred construction and design will result in a gradual triggering of the oxygen absorption system. Potassium sulfite is particularly well suited for use as an oxygen scavenger because it can be readily triggered by the retort process and has enough thermal stability to permit its use in thermoplastic processes such as injection molding.



To test the triggering mechanism for oxygen absorption a number of square plaques having five layers were assembled. Such a plaque was made as follows. The outer layers were cut from a 15 mil
5 (0.38 mm) thick polyolefin sheet which was a 50:50 melt blend of polyethylene and polypropylene. The central layer was a 2 mil (0.05 mm) sheet of ethylene vinyl alcohol co-polymer (GLD; as sold by Nippon Goshei Co., Ltd., Japan). The interleaving adhesive
10 layers were a modified polyolefin (Plexar; as sold by Chemplex Inc., Rolling Meadows, Illinois) into which was melt compounded finely divided potassium sulfite at a loading of 20% by weight. These adhesive sheets were about 2 mil (0.05 mm) thick. The separate layers
15 were stacked and then melt-pressed together to form an integral plaque in which the outer olefin sheets come together only at the edges to completely protect the innermost layers from ambient moisture. A further set of plaques were made in which di-sodium phosphate
20 was substituted for potassium sulfite in the adhesive layer. Because di-sodium phosphate does not absorb oxygen these latter plaques were used as a control.

The plaques were autoclaved at 250°F (121°C) for different periods of time and were then analyzed on
25 a MoCon oxygen permeability tester. In this instrument

both sides of the plaques can be purged with nitrogen gas. The gas stream from the lower side is passed over an oxygen detector. Under perfect conditions the reading from this detector should be zero; in practice leaks
5 cause a small reading, known as the baseline. Plaques which contain an active oxygen scavenger depress the baseline because the leaked oxygen is absorbed. This technique can be used to identify those plaques which are absorbing oxygen. Table 1 compares values obtained
10 under nitrogen gas purge for unretorted and retorted plaques.

TABLE 1

AGENT IN ADHESIVE LAYER	K_2SO_3								Na_2HPO_4	
Autoclaving time (mins)	0	0	30	30	45	45	60	60	120	120
Baseline reading (mV)	.03	.03	.02	.03	.02	.02	.02	.02	.03	.03

The results indicate that 30 minutes autoclaving is the borderline requirement to start the oxygen absorption
20 with this composition while autoclaving for 45 minutes triggers it.

For further testing, cylindrical-sided containers were thermoformed from multilayer co-extruded sheet. These containers had a diameter of 4 1/16" and a depth
25 of 4 7/16" (10.3 x 11.6 cms). The body of the container

consisted of six layers. The oxygen scavenger K_2SO_3 was mixed in a carrier material comprising high density polyethylene (HDPE) which was placed next to the inner polyolefin layer. The latter was a 50:50 melt blend of high density polyethylene (HDPE) and polypropylene (PP) structural layer. The multilayer structure of the container, from the inner surface to the outer surface, was as follows: 12 mil (0.30 mm) HDPE-PP/4 mil (0.10 mm) HDPE with 30% (by weight) K_2SO_3 /1 mil (0.02 mm) Plexar/2 mil (0.05 mm) EVAL/1 mil (0.02 mm) Plexar /12 mil (0.30 mm) HDPE-PP blend. PLEXAR is a Registered Trade Mark. EVAL is an ethylene vinyl alcohol co-polymer made by Kuraray Chemical Co., Ltd., Japan. A group of five layer containers omitting the K_2SO_3 layer were also prepared for control purposes. The layer composition for these controls was: 15 mil (0.38 mm) HDPE-PP/1 mil (0.02 mm) Plexar/2 mil (0.05 mm) EVAL/1 mil (0.02 mm) Plexar/15 mil (0.38 mm) HDPE-PP. The containers were filled with hot water (160°F, 71°C) and double seamed with metal lids containing two small rubber grommets. The head space between water in the containers and the lids was approximately 6/32 inch (4.76 mm) high.

At given storage times after retorting (at 250°F 121°C) or hot filling (at 160°F, 71°C), a sample of

head space gas was extracted through a grommet and analyzed for oxygen and nitrogen using gas chromatography. The oxygen concentrations in the head space (measured as a ratio of oxygen to oxygen plus nitrogen) are shown in Table 2. The concentration in the hot-filled but unautoclaved container is less than that of air (.21) because, as the hot water cools, its increased affinity for oxygen lowers the O₂ concentration in the head space.

Thus, it is clear that the autoclaved containers are triggered to absorb oxygen, since their head space oxygen levels fall as time passes while that of the unautoclaved container is steady with time. This further demonstrates the efficacy of the system for triggered oxygen absorption.

TABLE 2*

PROCESS	OXYGEN ABSORBING AGENT	STORAGE TIME, DAYS											
		.02	.04	.75	1	3	5	6	10	14	18	20	28
Hot fill	None			.19				.18		.18			.18
Hot fill	K ₂ SO ₃			.2				.19		.19			.18
Auto- clave, 30 Min	K ₂ SO ₃		.18		.15			.13		.08		.06	.05
Auto- clave, 2 hr	K ₂ SO ₃	.165				.11	.08		.045		.022		

*The numbers in the Table are oxygen concentrations in the head spaces.

TABLE 2A
O₂ CONTENT - cm³

		<u>Initial</u>	<u>3 months</u>
	No additives	10	34
5	K ₂ SO ₃	11	8

Table 2A shows data accumulated over a three-month period for containers retorted at 250°F (121°C) for two hours with results reported in Table 2 for the containers with K₂SO₃. These containers had been packed and retort processed with water and then stored for eighteen days. After this they were emptied and filled with 10 cc of water to maintain 100% relative humidity inside them. The head space above the water was filled with about 99% nitrogen and 1% oxygen. So filled and sealed, the containers were stored for 3 months in an environment comprising 100% oxygen at atmospheric pressure and 75% RH. For control purposes, a container without additives had the same processing and storage conditions. From Table 2A it is apparent that the K₂SO₃ scavenged container not only prevented permeation but also absorbed 3 cc of oxygen from the head space. The container without scavenger allowed 24 cc of oxygen to permeate into the container. The decrease of oxygen concentration in

the head space over the three month period conclusively demonstrates the scavenging effect of K_2SO_3 .

While the containers embodying the invention as
5 described above have a six layer structure, it may be preferred to employ fewer layers. For example, a five layer structure can be adopted wherein the potassium sulfite has been mixed into an adhesive layer. The system disclosed in detail above shows a prolonged
10 passive state which, thanks to its deliquescent behaviour, changes abruptly into its active oxygenphilic state. Other systems may have a less prolonged passive state and can also be exploited provided processing can be made to trigger a large change in the activity
15 of the oxygenphilic state.

One system which after triggering by water is an effective oxygen scavenger is a mixture of a heat treated gelatin and a strong alkali. Ordinarily, gelatin will not scavenge oxygen, but it will do so after a
20 heat treatment, either alone or in the presence of the alkali, at above $300^{\circ}F$ ($149^{\circ}C$) for more than 5 mins.

The following examples illustrate the effectiveness of this system. The composition used for the examples is 10% (by weight) Type A gelatin and 20% (by weight)
25 NaOH in a 70% (by weight) carrier consisting of Plexar. The said composition was blended together in a Brabender

mixing head at 400°F (204°C) for 20 minutes, and then pressed into approximately 2 mil thick films.

The film is capable of rapidly scavenging 170 cc oxygen per gram of gelatin when the film is saturated with moisture. One of the conditions adequate for saturating said composition is to retort the bare film at 250°F (121°C) for 2 hours.

The oxygen scavenging rate is extremely slow if the film of this gelatin composition is protected by a moisture barrier to reduce moisture peratration into the said composition. The following table illustrates the unretorted oxygen scavenging rate of the film of the gelatin composition protected by a 15 mil (0.38 mm) HDPE layer (moisture barrier layer) on both sides.

15

TABLE 3

cc O₂ Scavenged per gram of gelatin
(73°F 22.8°C)

Storage Time Storage RH	37 Days	58 Days	108 Days
44%	0	6	8
75%	0	10	41
100%	9	24	61

It is apparent that the O₂ scavenging rate of the said composition can be controlled by the moisture protective layer and the storage conditions. Absorption will take place after the materials are exposed to moist air for
5 prolonged periods of time. This shows that while retorting gives an immediate triggering, it is also possible to obtain triggering without retorting.

The gelatin containing system is effective as an oxygen scavenger but produces unpleasant odors when
10 exposed to elevated temperatures for prolonged periods of time. Where containers are to be made by melt processing plastics (containing the present oxygen scavenger systems), it is preferred to use a thermally stable system such as potassium sulfite as the oxygen
15 scavenger.

The constructions described above have had the oxygen barrier layer at or near the center of the laminate, flanked on either side by a structural (polyolefin) layer. There are alternative constructions
20 which will perform satisfactorily, and are within the framework of this approach. One example is a multilayer structure with thin layers of an oxygen barrier on the outside. The bulk of the sidewall would be a structural plastics layer in which an oxygen scavenger is embedded.
25 The structural layer serves as the means to protect the oxygen scavenger lying within the structural layer

from premature triggering, though a fractional amount of the oxygen scavenger near the surface of the structural layer may be triggered before product is packaged. Such a can or package could be made with
5 a polyolefin wall containing a potassium sulfite dispersion and a Saran or epoxy coating on the outside. Although outer oxygen barrier layers are preferred they can be omitted or replaced by pure polyolefin. In this case more scavenger would need
10 to be embedded in its host or structural layer. Finally, a chip instead of a pellet or package of powder, could be used by placing it within a sealed container. An advantage of integral constructions is that they avoid the problem of packages of dry
15 powder rupturing and contaminating the packed product. The chip could be of any of the recited constructions, the choice depending on the application.

While a preferred system has been shown and described it should be appreciated that there are many
20 other deliquescent compositions and polymeric materials which will, when used in combination, exhibit the requisite triggering ability to an oxygenphilic state and hence permit the successful application of the mixture to packaging for the commercial processing
25 of comestibles.

Multilayer structures comprising an oxygen barrier associated on at least one side thereof with a structural layer embodying an activatable oxygen scavenger can be of flexible or rigid character.

- 5 Flexible structures can be used to fashion sachet or bag type food packages, while rigid structures can be used to produce plastics containers for instance having the familiar shapes associated generally with food or beverage cans.

Claims:

1. An oxygen-absorbing structure for use in protecting the contents of containers against oxidation, wherein the structure includes an oxygen barrier layer
5 which is substantially impermeable to the flow of oxygen therethrough, characterised by a composition, disposed in operative relation to at least one of the opposite surfaces of the oxygen barrier, which has a first state wherein said composition is substantially passive
10 and will not absorb oxygen and has a second oxygenphilic state wherein it chemically combines with oxygen, and means disposed in protective relation to the composition which selectively permit a change from the first passive state to the second oxygenphilic state.
- 15 2. A structure according to claim 1, wherein the said composition is in its passive state when dry and can change to the oxygenphilic state when wet.
- 20 3. A structure according to claim 1 or claim 2, further characterised in that the composition-protecting means includes a plurality of protective polymeric layers substantially resistant to the permeation of moisture therethrough at temperatures below 100°F (37.8°C), the layers allowing enhanced transmission of moisture above 200°F (75.6°C), and the said composition

being in a protected position between the polymeric layers.

4. A structure according to claim 3, characterised by the polymeric layers being of olefinic material.

5 5. A structure according to claim 4, characterised by the olefinic material being a melt blend of polyethylene and polypropylene in substantially equal proportions by weight.

6. A structure according to any of claims 1 to 5,
10 characterised by the said oxygen barrier being an ethylene-vinyl alcohol co-polymer and by the said composition being sandwiched between the oxygen barrier and the composition-protecting means.

7. A structure according to any of claims 1 to
15 6, wherein the said composition contains a deliquescent substance.

8. A structure according to claim 7, wherein the said composition contains a sulfite salt that becomes oxygenphilic when in a deliquescent state.

20 9. A structure according to claim 8, wherein the salt is potassium sulfite.

10. A structure according to any of claims 1 to 6, characterised by the said composition being a blend of an alkali and gelatin wherein the gelatin
25 has been heat treated in the presence or absence of the alkali.

11. A structure according to claim 10, wherein the heat treatment consists of raising the temperature of the gelatin alone or the blend with the alkali to greater than 300°F (149°C) for more than 5 minutes.

5 12. A structure according to claim 10 or claim 11, wherein the alkali is sodium hydroxide.

13. A plastics structure having enhanced resistance to oxygen transmission therethrough, characterised in that the structure includes at least
10 one layer of a polymeric substance which includes a composition which, in a dry condition, is substantially passive and will not absorb oxygen and which, in a moist condition, is capable of exhibiting an active, oxygenphilic state for scavenging oxygen in the course of
15 transmission through the structure.

14. A structure according to claim 13, characterised by the polymeric absorption layer comprising a polyolefin having potassium sulfite distributed throughout.

20 15. A structure according to claim 13 or claim 14, characterised by being in the form of a polymeric chip for inclusion in a sealed package for absorbing oxygen therein, the chip having the said composition distributed uniformly therein.

25 16. A multi-layer container having a wall

incorporating the structure claimed in any of claims
1 to 14.

17. A container according to claim 16,
characterised by a wall including an outer olefinic
5 layer, an oxygen barrier layer, a polymeric layer
including the said composition and an innermost olefinic
layer, the olefinic layers or a further layer or layer
of the wall being impermeable to moisture for protecting
the said polymeric layer therefrom at temperatures
10 below retorting temperatures, but being permeable to
moisture at the latter temperatures for activating the
said composition to an active, oxygenphilic state.

18. A method of protecting an oxidisable
product from degradation through oxidation in storage,
15 characterised by the steps of fashioning a container
from a plastics structure which has at least one layer
of a polymeric substance including a moisture-
responsive material which is activatable, to an
oxygenphilic state to absorb oxygen, under predetermined
20 conditions, filling the container with the product and
hermetically sealing the container about the product,
and subjecting the sealed container to high levels of
moisture for a preset period of time to activate the
said material to absorb oxygen within the container.

25 19. The method according to claim 18,

characterised in that the last step is performed by a high temperature sterilization process, the product being a comestible.

20. A method of making a container, comprising
5 laminating a plural layer plastics structure from two structural outer layers and two inner layers therebetween, one inner layer comprising an oxygen barrier and the other comprising a polymeric layer containing a triggerable composition which exhibits a first, passive
10 state substantially incapable of absorbing oxygen when dry, and a second oxygenphilic state wherein it reacts chemically with oxygen, the composition being triggerable to the second state under predetermined conditions of moisture or moisture and heat, and thereafter shaping
15 the laminated structure into a container.

21. A method of making a protective element for guarding contents of containers against oxidation in storage, comprising the steps of incorporating in a polymeric meterial an oxygen scavenging composition
20 and forming a chip element from the resulting plastics combination for inclusion in a container, said composition being triggerable from a first, passive state substantially incapable of absorbing oxygen when dry to a second oxygenphilic state wherein it reacts chemically
25 with oxygen when exposed to predetermined conditions of moisture or moisture and heat.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
A, D	GB-A-2 000 431 (TOPPAN PRINTING) * claims 1,7,8; page 1, line 1 - page 3, line 31 * & DE - A - 2 827 247	1,7-9	B 65 B 55/19 B 65 D 81/26 A 23 L 3/34 B 32 B 27/18 C 08 K 3/30
A, D	WO-A-8 100 230 (AMERICAN CAN) * claims 8-11,17-21; page 11, line 1 - page 12, line 26; examples 1,3 *	1,3-6, 16-18, 20	
A, D	US-A-4 048 361 (E.I. VALYI) * claims 1,6-9,11-15; column 1, line 62 - column 5, line 35; figures 2-4 *	1,3,4, 13,14, 16,21	
A	US-A-3 712 848 (W.P. CASEY et al.) * the whole document *	1,3,4, 14	
A, D	US-A-4 113 652 (Y. YOSHIKAWA et al.) * claims 1,3; column 2, line 23 - column 3, line 63; column 5, line 18 - column 6, line 10 *	1,2,7- 9	A 23 L B 65 B B 65 D B 32 B C 08 K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 01-09-1982	Examiner BLASBAND I.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. *)
A, D	US-A-2 825 651 (C.C. LOO et al.) * claims 1,3,6,14-16; column 2, line 39 - column 3, line 4; column 4, line 28 - column 5, line 11; figure 1 * -----	1,8,9, 15,21	
			TECHNICAL FIELDS SEARCHED (Int. Cl. *)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 01-09-1982	Examiner BLASBAND I.
CATEGORY OF CITED DOCUMENTS			
X . particularly relevant if taken alone Y . particularly relevant if combined with another document of the same category A . technological background O . non-written disclosure P . intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D . document cited in the application L . document cited for other reasons A . member of the same patent family, corresponding document	